REMOVAL OF CONGO RED DYE FROM WATER USING ORANGE PEEL AS AN ADSORBENT

Thesis Submitted by

ROSHAN SAHU (111CH0401)

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Dr. SUSMITA MISHRA

DEPARTMENT OF CHEMICAL

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Certificate

Department of Chemical Engineering
National Institute of Technology
Rourkela -769008, India

This is to certify that, Roshan Sahu, a student of B.Tech, th Semester, Chemical Engineering Department, NIT Rourkela bearing Roll No. 111CH0401 has completed his final project on the topic "*Removal of Congo Red Dye from Water Using Orange Peel as an Adsorbent*" under my guidance successfully. He has shown an authentic work with valid results and submitted a complete thesis of the work as required according to the curriculum in partial fulfillment for the award of B. Tech. degree.

Date: ……

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Dr. (Mrs.) S. Mishra,
Associate Professor,
Chemical Engineering Department,
NIT Rourkela.

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Date- ……

Roshan Sahu
Roll no. 111CH0401

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ABSTRACT

The aim of this project work undertaken by me is to study the removal of Congo red dye from water using orange peel as an adsorbent. The need for using Cheap and eco-friendly adsorbent for removal of congo red dye from aqueous solution is of paramount importance. Batch operations were carried out in liquid phase to observe the effect of various experimental parameters such as pH, contact time, temperature, initial concentration of congo red, adsorbate dose and the optimum conditions for these parameters were evaluated. Various characteristics of the orange peel sample were also examined. Study of adsorption isotherms was carried out and best fitting models for isotherms were suggested.. The Langmuir and Freundlich isotherms were used to fit the equilibrium data and the results showed that the Freundlich isotherm seemed to agree better than the Langmuir isotherm. The outcomes indicated that orange peel can be used as a good low cost alternative for treatment of effluents containing congo red in water.

KEY WORDS: adsorption, dye, orange peel, isotherm,desorption

Chapter 1
Introduction

1. INTRODUCTION

1.1 Depletion of Fresh-water resources

The interest for fresh water assets is accelerating, and rivalry for fresh water is progressively of concern to organizers and policy makers. At present 70% of the world's fresh water withdrawal is utilized by farming, while 20% is utilized as a part of industry and just 10% is utilized for civil utilization. The anticipated development of urban populaces will build stress on water assets for urban consumption, while expanding the interest for fodder generation in far off ares to bolster urban connected industrial animal production systems. The interest for fresh water assets has surpassed populace development by an element of two or all the more throughout the most of the recent hundred years[34]

The UN estimates that the amount of water released as waste annually is about 1,500 km3 , six times more water than exists in all the rivers of the world. (UN WWAP 2009). Therefore the first logical step in tackling this mammoth of a problem is reclamation of fresh water from these water which is released as waste. [35]

The textile industry is one of the largest polluters in the world. World Bank estimates that nearly 20% of all global industrial water pollution comes from the treatment and dying of textiles. The dye that we have worked with i.e. Congo red is a grave sinner when it comes to polluting the environment. It is known to cause anaphylactic shocks in humans and is potentially carcinogenic. The dye discharged in water bodies without being treated properly, disrupts the cycle of life of aquatic animals and plants by obstructing the penetration of sunlight

WHO prescribes a limit of 1 microgram/litre of colouring substances in drinking water. The methods that are currently used for the remediation of dyes in waste water are chemical oxidation, adsorption by activated carbon, microbial methods. They all have their advantages and disadvantages cited in table 1 (a) along with their advantages and disadvantages

Our objective here is to use such naturally available waste materials that can be suitably applied to remediate dye contamination(congo red) in waste water.

1.1 Objective of the present work

The objective of this project work is

- To explore the feasibility of orange peel for the removal of congo-red dye from aqueous solutions
- To characterize the adsorbent by proximate analysis, SEM, and BET surface areas
- To determine the various physiochemical controlling factors that affect adsorption including pH, adsorbent concentration, initial concentration of dye, time of contact and temperature..
- To define the practicability of various Isotherm models for the best-fit Isotherm equation.
- To carry out desorption studies to investigate the amount of recoverable dye from the used adsorbent

Chapter 2
Literature Review

2. LITERATURE REVIEW

2.1 Water Pollution

The presence or introduction of undesirable materials in the earth which have destructive or toxic impacts is defined as Pollution. It is the presentation of contaminants in the surroundings which have adverse impacts. There are various manifestations of pollution which exist nowadays like air pollution, water pollution, and clamor pollution. The distinctive constituents of pollution which are called pollutants may be either contaminants which are as of now in nature or those which have been gone onto presence because of human exercises. Pollution may exist as any natural or inorganic materials or at times some form of energy like sound, light and so forth.[37]

Water pollution has become one of the most dangerous threats to the environment in today's world. It is the degradation in quality of water resources-rivers, oceans, groundwater etc. because of human beings and their activities. There are various ways by which water gets polluted, most important being the discharge of industrial waste water through spillage from into water bodies[37]. The sewage discharge from homes is not subjected to proper treatment before being discharged to the environment. This serves as the main cause of pollution. Other causes include chemicals which are flowing on the surface due to various activities and fertilizers and pesticides release from the agricultural activities.

Thus we can come to a conclusion that any kind of change in properties of water which may be physical, chemical or biological and which have harmful consequences is water pollution. The effects of water pollution are not just limited to human beings, but it is fatal for the entire ecosystem. Water comes from many sources like ground water, surface water, that is why the cause of its pollution are different depending on the sources. Chemical, textiles, tannery industries etc. cause high rate of pollution [37]. The effluent containing heavy metals, chemicals, dyes, oils and many other harmful materials are discharged by the industries into the water bodies without proper treatment, thus leading to contamination of water bodies. The horrific effect of water pollution can be easily guessed by the fact that today, polluted drinking water has become a chief concern for mankind. There are more than 300 million cases of water-borne diseases every year with the number showing no signs of dwindling in the near future, which leads to the death of around 8 to 12 million people. In developing countries like India, Pakistan and Bangladesh more than 60 percent of harmful wastes are thrown into water bodies where they contaminate the water available for use. Approximately 600 persons in India die of water pollution related illness every day[37] . Due to these catastrophic effects of water pollution, it has become a matter of ultimate importance to find out

different methods for treatment of waste water owing to the great importance of pure water for the existence of mankind.

2.2 Dyes

A dye is a coloring substance that has a inclination to adhere to the substance to which it is applied. In most of the cases, the dye is applied in the form of a solution in water. For better performance of dye on the cloth fiber, some additional substances called mordants are used which improve its bindability. Both dyes and pigments appear to be colored because certain wavelengths of light are absorbed more than others. There are various reasons because of which dye act like they do; the most basic reason being that it absorb wavelengths in the visible spectrum (400–720 nm) [37].Also because they contain chromophores which are colour-bearing group. Also, the structure of dyes contain alternate double and single bonds the last reason being that dyes shows resonance property which is the most important stabilizing factor in organic compounds .The chemical substance loses its colour when any of these properties are not satisfactorily present in them. Dyes likewise contain another substances called auxochromes which are called shading partners. Carboxylic , sulfonic and amino acids, and hydroxyl groups are few of the auxochromes. These auxochromes are not sensible for the shading of the colorant but rather are utilized to change the dye solubility. Pigments are likewise shaded substances yet they are not the same as dyes in the way that they ordinarily are insoluble and tends to join to. The dyes are categorised as natural or synthetic/simulated. The colorants which are gotten from plants, minerals or any commonly happening substances are categorized as Natural dyes. Most astounding rate of natural dyes are gotten from herbal sources like roots, leaves, bark and wood of trees. Expanded interest for promptly accessible, reasonable, and effectively applied dyes prompted the innovation and quick development of synthetic/ man made dyes [37].

The occurrence of dye or colouration and its favorable compounds have forever been unwanted in water for the use in either domestic or industrial requirements. Colour may be a visible unwanted product. Various kinds of dyeing materials like dyes, tanning, lignin, inorganic pigments etc. all impart colour. Midst complex industrial sewage with numerous sorts of dyeing materials, dye wastes form a major part. At present more than 8 thousand various kinds of dyes are readily available in the shops having different properties chemically. The pharmacological manufacturing industries, dye and dye intermediates industries[1], paper and pulp industries[3], , Kraft bleaching[2] are different industrial sectors that employ the use of dyes. Other industries include tannery[4] ,fabric industries[5] ,cosmetics, paper, rubber etc. Colour of a dye is mainly because of the intermediates of dye and organic colorants[7]. Colour removal from

industrial effluents is one amongst the foremost and the toughest demand faced by the paper and pulp industries, textile finishing, dye producing, attributable to noxious nature of dyes. According to the ionic structure in it, dyes are mainly categorized in three categories: (a) reactive and direct acid dyes (anionic), (b) basic dyes (cationic) and (c) all dispersed dyes (nonionic).

2.3 Harmful Effects of Dyes

All the wastes of the colourant category produced from various types of industries might have injurious impacts on microbial inhabitants and may be unhealthful and sometimes even fatal to mammals. These dyes may source for eczema, irritation of skin problem, mutations and cancer. Few chemicals used to produce dye are highly toxic carcinogens or hormonal disrupters. The excessive use of dyes causes problems relating to ecosystem in the environment. This not only solely reduces the ability of sunrays to penetrate into water and decreases photosynthetic activity but also results in causing difficulties within the atmosphere[37].

Congo red is an unsafe dyes which not only possess extremely toxic properties affecting the cells of mammals but also possesses the power to cause anaphylactic shocks in humans and is potentially carcinogenic. The dye discharged in water bodies without being treated properly, disrupts the cycle of life of aquatic animals and plants by obstructing the penetration of light[8] . They cause decrease of dissolved O_2 due to combined increase in the biological oxygen demand (BOD) to sustain aquatic life. Since some dyes are terrible cyanogenics, they cause direct damage or reticence of their chemical action abilities[37]. At low concentrations, dyes have an adverse effect on the life of marine animals and therefore, the cycle of food. As per their design, dyes are relatively very steady molecules, created to fight against the ruin by light, biological, chemical and other natural modes of degradation[9].

These days approximately a million metric tons of dyes are produced annually in the world of azo dyes (R1-N=N-R2), which signify about 72% of the total dyes [10]. About 60,000 metric tons of dyes are being produced in India annually, which is very close to 6.6% of entire production of the world. According to the recent survey, about two third of its market are being used in textile industries[11]. It has been indicated that 14% of the non natural textile dyes used every year are disposed off to water streams. Waste water treatment plants are the major sources of the addition of these to the environment[12]. Due to the stability and complexity in structure of dyes, it is very difficult to decolorize dyes, which make it compulsory to get rid of them from industrial sewages before disposing them off into the main stream[13].

The effluent from a dye industry usually contains 0.5–0.8 g dye per litre[14].

2.4 Removal Methods

Thus, the removal of this colour is a herculean task for the fisheries industries, textile finishing, dye producing, Kraft bleaching and tannery industries and pulp and paper among others. Chemical oxidation, membrane separation etc. are the various ways used to remove dyes from waste water. Other processes include aerobic/anaerobic processes, electrochemical methods, agglomeration etc. Because of being expensive and relatively inefficient, most of these processes are not used on large scale[15]. Coagulations and chemical and electrochemical oxidations have low practicability on large scale plants[15] . Adsorption is preferable over the above mentioned processes and is widely used because of low cost and high performance. Activated carbon is the most commonly used adsorbent . Metal hydroxides, alumina, silica etc. are other common ones. Economic benefits, performance efficiencies and environment are primary considerations while choosing an adsorbent, therefore researchers usually cheap and best adsorbents, which are usually waste materials such as char [15].

Activated carbon is being used as an absorbent in most of industrial systems use for removal of dyes in wastewater attributable to its notable adsorption capability[16-18]. However because of the fact that activated carbon is deemed to be expensive, adsorption is preferred by using cheaper materials. Various literature studies have shown that many relatively cheaper constituents are been successfully used for excluding dyes from their solutions in water. However, very few of those can be utilized well to separate the colorant from the waste water stream. Therefore, through this project the potential of yet one more new waste matter (orange peel) which is handily available in abundance in our country India has been explored.

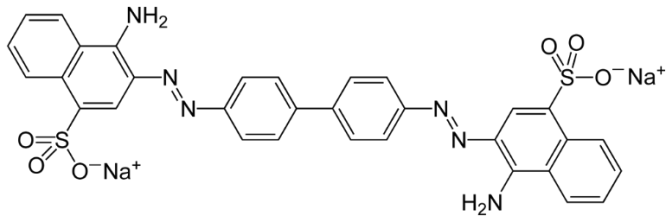
2.5 Synthetic Dyes

The dyes which are not natural and are created by people are called engineered or artificial dyes. They grant better properties to the materials they are acted upon and are likewise economic furthermore have boundless alternatives to be browsed. Because of these properties, they have supplanted the common dye in a short compass of time. Today, the situation is such that we can see engineered dyes all over, extending from paper, cosmetics, garments and numerous more. They are additionally utilized as a part of elastic commercial enterprises, beauty care products and so on. Yet, despite the fact that with such a large number of focal points,

engineered dyes are exceptionally destructive for humanity and for the environment. That is the reason there are number of systems being connected these to particular these dyes from water. In any case, most the courses of action utilized are exorbitant and not exceptionally powerful. The advantages and restrictions of diverse treatment techniques other than rising technologies are given in Table 1(a) and 1(b).

2.6 Congo Red

Congo red dye is the adsorbate, its colour is red. It gives red colored solution in aqueous phase at Ph >5 and the color changes to blue at more acidic pH. It is a acidic anionic dye and has chemical formula as $C_{32}H_{22}N_6Na_2O_6S_2$. The molecular weight of congo red dye is 696.663219, λmax = 510 nm. Its molecular structure in 2 dimensions is as follows



2.7 Adsorption

Adsorption is the process in which different molecules, ions and atoms of a gas or a liquidget attached to the surface[19] .Adsorbate is attached in the form of a film on the surface of the adsorbent. This process is different from absorption since in absorption, the substrate which is usually in the form of fluid percolates into the absorbent[20]. Thus absorption includes the whole matter whereas adsorption is only effective on surfaces. But both the terms are included in a single term called “sorption”, and the reverse of “sorption” is called “desorption”. Adsorption is proving to be a better and more efficient method of waste water treatment in recent years. It is the process of deposition of a layer of solid or gas on the substrate. Thus in the process of adsorption, the colouring substance gets separated from fluidic phase and gets accumulated on the solid phase substrate[21].

2.8 Mechanism of adsorption

Adsorption process involves three steps. First of all, the substance which has to be adsorbed i.e. adsorbate enters in to the outer surface of substance which adsorbs it i.e. adsorbent[22]. After that, the adsorbate move into the openings/pores of the adsorbent particles. Higher the surface area of the pores,

higher will be the adsorption .And finally the molecules get attached to the surface area of adsorbents. .Thus the process of adsorption is a surface phenomenon. It occurs because of the interparticle forces of attraction between molecules or ions of adsorbate and adsorbent[22].

2.9 Adsorbate

The adsorbate used, Congo red is an organic compound that is used in various industries like textiles and paper as dyestuff. It was the first synthetic dye that could attach itself without the use of a mordant Created in 1884 it is the first member of a group of azo dyes derived from benzidineand has been used as a colouring material in the textile and paper industry since long.

In actual form, Congo red refers to $C_{32}H_{22}N_6Na_2O_6S_2$, Congo red has a tendency to aggregate in aqueous as well as organic solutions. The proposed mechanisms propose interactions of the hydrophobic nature between the aromatic rings of the dye molecules, leading to a pi–pi stacking phenomenon. Although these agglomerates are present under various sizes and shapes, the "ribbon shaped micelles" of a few molecules appear to be the principal form). This agglomeration phenomenon is more prevalent in high Congo red concentrations, at low pH and/or high salinity.

The reactions involved are as follows.

- Benzene → Nitrobenzene(by nitration) → Hydrazobenzene(by zinc and sodium hydroxide) → Benzidine hydrochloride(by HCl)
- Napthalene →Alphanitro naphthalene (by nitration) → Napthionic acid (by sodium bisulphite)
- Benzidine Hydrochloride → biphenyl bis-diazonium chloride(by HCl and Sodium Nitrite)→ Congo red(Sodium napthionate)

The equilibrium analysis of the isotherms and the kinetic study for the removal of congo red dye from aqueous solutions by adsorption using pulp fly ash and activated carbon has been studied. Adsorption studies were conducted in batch form to examine the impact of different parameters on dye removal. The parameters included like contact time, adsorbent dosage, pH, and the initial concentration of congo red. The strong effect of solution's initial pH was found on the chemistry of each-the dye molecules as well as the adsorbents in the solution. The equilibrium contact time came out to be 2 hour.. The second order kinetics has been followed.

The use of deoiled soya which is an agricultural waste has been also used for the congo red removal and recovery. Batch adsorption techniques were used for primary study including concentration of deoiled soya, contact time, sieve size etc[23]. IR and DTA curves were used for the characterization of the adsorbent.

Freundlich and Langmuir models suggested the sustainable mechanism of the involved process involved. The rate constant is relevant to first order rate expression which was determined after finding out specific rate constant Thermodynamical parameters have also been calculated [23]

In the study based on "Removal of dyes from aqueous solutions by cellulosic waste orange peel", the study has been conducted on three different dyes- Rhodamine-B, Procion orange and Congo red,by waste orange peel. The initial pH of the solution, adsorbent dosage etc. were examined. Two isotherm models- Freundlich and Langmuir were being obeyed by the adsorption process .The uptake capacity was found to follow "first-order" rate kinetics [37]. Low pH was favorable for all the three dyes' adsorption. In contrast, the study of desorption experiment showed alkaline pH to be efficient for desorption[26]. The adsorption of congo red dye using bentonite as adsorbent in a batch absorber has also been studied and the various effects of parameters of adsorption onto bentonite has been found out. The removal of dye was found to boost with increasing contact time till a stage of equilibrium was reached and initial dye concentration and also the sorption capacity of adsorbent used as well as the initial pH range of 3-11[27]

The "Removal of congo red from aqueous solutions by adsorption on oil palm trunk fiber" was carried out where the variables which were operating were concentration of dye initially, contact time for adsorption and pH. The multilayer adsorption isotherm, the Langmuir and the Freundlich isotherm were used to analyze the data of equilibrium adsorption. With increasing concentration of congo red dye, the pore-diffusion coefficient was enhanced whereas the film-diffusion constant was diminished [29].

Yet another "Biosorbent- neem sawdust" has also been used to act as an adsorbent for the "removal of congo red dye from an aqueous solution". Varied conditions of experiment like time needed for efficient agitation, concentration of dye, adsorbent dosage, pH of the solution to estimate "the potential of neem sawdust for the removal of congo red dye from wastewater". As the initial concentration of dye is decreased and the adsorbent dosage increased, the percent removal of dye also increases[37].

Still another "coir pith" has also been studied to remove congo red from waste water. Proper physiochemical optimization has been carried out to oust congo red from its aqueous solution including effect of contact time, effect of pH , concentration of dye, amount of adsorbent used to investigate the potential of extraction of congo red dye from waste water. The reported findings show remarkable promise in the future use of this as a a low cost adsorbent for the removal of dyes from waste water but the recovery potential via desorption is very low in this case[35]

Bagasse fly ash (BFA) (generated as a waste material from bagasse fired boilers) and the use of activated carbons—commercial grade (ACC) and laboratory grade (ACL), as adsorbents for the removal of congo red (CR) from aqueous solutions has been studied here. Batch studies were conducted to evaluate the adsorption capacity of BFA, ACC and ACL and the effects of initial pH (pH_0), contact time and initial dye concentration on adsorption. The pH_0 of the dye solution strongly affected the chemistry of both the dye molecules and BFA in an aqueous solution. The effective pH_0 was 7.0 for adsorption on BFA. Kinetic studies showed that the adsorption of CR on all the adsorbents was a gradual process. Equilibrium reached in about 4 h contact time. Optimum BFA, ACC and ACL dosages were found to be 1, 20 and 2 g l^{-1}, respectively[36]

Table 1(a): Available Methods for treatment of dyes [37]

Treatment Methodology	Stage of treatment	Type of Industry	Advantages	Limitations
I. Physical Methods				
1.Adsorption				
a. Activated Carbon	Pre/post treatment	Brewery/tannery/textile	Economical, good removal efficiency	Regeneration is costly
b. Bagasse	Pre treatment	Sugar/Brewery	Waste recycling	Post treatment disposal
c. Peat	Pre treatment	Any industry	No activation required	Lower surface area
d. Wood chips	Pre treatment	Any industry	Good adsorption for colourants	Huge quantity required
2.Irradiation	Post treatment	Kraft mill, paper and pulp	Effective removal at low volumes	Requirement of dissolved Oxygen
3.Ion Exchange	Main treatment	Any industry	Low cost regeneration	Limited applications
II. Chemical Methods				
1.Oxidation				
a. Fenton's Regeneration	Pre treatment	Textile	Wide range of decolourization	Expensive
b. Ozonation	Main treatment	Brewery/Distillery	Effective for both soluble and insoluble dyes	Unsuitable for dispersed dyes
c.Electrochemical oxidation	Post treatment	Kraftmill		Cost intensive
2.Coagulation	Pre treatment	Sugar/Pulp and paper	Low capital costs	Dewatering and sludge handling problems
III. Biological Methods				
1.Aerobic Process	Main treatment	Kraftmill/Tannery	Colour as well as COD removal	Longer detention time needed.
2.Anaerobic Process	Main treatment	Pulp and paper/sugar/distillery	Biogas produced for steam generation	Longer acclimatization phase
3.Single Cell(Fungal, Algae/Bacterial)	Post treatment	Any industry	Good removal efficiency for low concentrations and volumes	Cost intensive, unable to treat large volumes

Table1 (b): Emerging technologies for treatment of dye [37]

Treatment Methodology	**Stage of treatment**	**Type of Industry**	**Advantages**	**Limitations**
1.Advanced Oxidation Process	Main treatment	Distillery/Textile	Insurance of mineralization, enhances biodegradability	Expensive process
2.Membrane Filtration	Main treatment	Brewery/Tannery	Wider application for complex wastes	Dissolved solids are not separated
3. Photocatalysis	Post treatment	Any industry	Shorter detention times, atoxic and inexpensive	Effective only for small amount of colourants
4.Engineered Wetland Systems	Pre/post treatment	Any industry which release large volumes of effluents	Can be operated on large volumes of water cost effectively	Difficult to manage during rainy season, high installation cost
5.Enzymatic Treatment	Post treatment	Any industry after biological treatment	Unaffected by shock loadings, effective for specifically selected compounds	Tedious work of isolation and purification of enzyme, presence of interferences
6.Sonication	Pre treatment	Any industry	Simple in use, very effective in integrated systems	Relatively new method, full scale application is still awaited
7.Redox Mediators	Pre/supportive treatment	Any industry after biological treatment	Easily obtainable, improves the procedure by increasing the efficiency of electron transfer	Dependent on biological activity of the system

Chapter 3
Materials and Methods

3.1 MATERIALS

3.1.1 Instruments

Table 2 gives the list of instruments used in this project work, their manufacturers, functions and the operating conditions

Table 2: List of Instruments

Instrument	Manufacture	Function	Operation conditions
Analytical balance	Sartorius (BS223S)	Weight measurement	1mg - 100g
pH meter	Systronics (361)	Measurement of pH	pH 1 to 12
Incubator shaker	Environmental orbital Shaker	Shaking of conical flasks containing samples	• Speed: 120 rpm. • Temperature: 25°C-40°C.
Scanning Electron Microscope	JEOL (JSM-6480 LV)	To study the clear morphology about the structure and extent of Orange peel samples.	• Magnification: up to 10000X • Resolution : 1µm • Detector: Everhardt Thornley secondary electron detector and Solid state Backscattered detector.
Micro Centrifuge	Remi (RM12C)	Separation of undissolved dyes from the solutions	• 8000 RPM for 10 min
Brunauer–Emmett–Teller (BET) Surface Area	Quantachrome Instruments	To determine the surface area and pore size of the sample.	• Degassing of N_2 gas at • 70 ^{o}C
UV-vis Spectrophotometer	Labindia	To determine the absorbance	• Wavelength-582nm
Hot Air Oven	WEIBER	For drying of samples	• Done at 70°C for 8 hours maximum
Oven and Furnace	WEIBER, ADCO Electric furnace	For proximate analysis: ASTM-D-3172,3173,3174,3175	• As per standards

3.1.2 Chemicals and Glasswares

All reagents utilized amid the project work were of analytical grade and all arrangements were carried out utilizing distilled water. Glassware utilized for the analyses i.e. volumetric flasks, pipette, weighing cylinder and so on are all made of of Borosil and are acquired from Tarson Product Private Limited. All the dishes were washed altogether with water a few times (faucet water) and followed by washing with distilled water lastly were dried in hot air oven to evacuate any hint of moisture present.

3.2 METHODS

3.2.1 Preparation of Adsorbent

Oranges are found in plenitude in India. Their peels can undoubtedly be acquired from any juice shop. Since peels does not have any critical utilization, they are dealt with as waste materials and hence are accessible in bounty at free of expense. As a matter of first importance the orange peels were altogether washed to get rid of dirt and undesirable particles stuck to it. They were cut it little pieces for making it simple to crush them. The little bits of peels were kept in hot air oven at a temperature of 70 ^{0}C for 8 hours .After drying, the pieces were pulverized in a mixer grinder until they got to be fine powder. The powder was sieved so that all the particles to be utilized are of uniform size. Finally the orange peel powder was stockpiled in air tight container so they can be utilized in the future without any further treatment.

3.2.2 Adsorbate

.The aqueous solutions of varied concentrations of congo red dye was prepared by dilution from its stock solution and the study were done by varying different parameters like contact time , pH, amount of adsorbent used, and initial concentration of the solution

3.2.3 Experimental Procedure

Batch techniques were utilized to study the adsorption of congo red dye using orange peel powder**.** Firstly, the stock solution of 1000 mg/L of dye was prepared by dissolving 1000mg of congo red dye in 1000 ml water. Water has been used to dissolve congo red particles effectively in the solution. First of all, two dye solutions of concentration 20 ppm each were prepared from the stock solution and 1gram of adsorbent i.e. orange peel powder was added to one of them. The solution with adsorbent was kept in the shaker for 120 minutes at 120rpm under normal conditions. After the passage of 2 hours, it was taken out and allowed to centrifuge at 8000rpm for 10minutes to separate all the undissolved particles. Then both the solutions-the solution with adsorbent and the one without the adsorbent were analyzed in a UV-vis spectrophotometer at maximum absorbance. The results obtained from the spectroscopy confirmed that the considerable amount of dye was adsorbed on adding orange peel powder. Thus the further studies were feasible.

Here it is important to mention that we tried to study the scope of sweet lime too for the removal of congo red dye from water. Sweet lime in the powdered form was mixed in one of the solutions just as the orange peel samples as mentioned above. But the results were not satisfying and we came to conclusion that sweet lime cannot be used as adsorbent for the removal of congo red and thus we further focused our study only on orange peel adsorbent. However that when we tried to separate the dye particles which were undissolved from the solution by filter paper, then the paper also adsorbed some of the dye during the process. This affected the final readings in the spectroscopy. Thus for our whole project, we used centrifuge instead of using filter paper. Furthermore, first of all we prepared five workings solutions of varying concentrations from 10-40 ppm.The same procedure was applied and the results were

plotted to get the calibration curve. This curve served the basis for all future calculations during the complete project work.

3.2.3.1 Study of contact time

A dye solution of 20mg/l was set by diluting the stock solution. This solution was maintained at a pH of 4.5 and 1gram of adsorbent was added to it. Then the solution was kept in shaker for 140 minutes at room temperature. The solutions were taken out at different intervals of time. And finally, all the samples of different time intermissions were examined and compared with the initial sample which was without adsorbent to find out the percent removal of dye and the effect that contact period has on it.

3.2.3.2 Study of pH

Five working solutions of 20mg/l concentration each were prepared from the stock solution. They were kept at different pH ranging from 4-10 by adding 0.1N HCl or NAOH. Again 1 gram of the adsorbent was added to each of them and kept in shaker at room temperature and at 120 rpm for 2hours.The solutions were taken out after a period of two hours and centrifuged at 8000 rpm and studied in UV-vis spectrophotometer to compare the result.

3.2.3.3 Study of adsorbent Dosage

Typical dye solutions of 20mg/l were set once again from the stock solution. To each one of these solutions, varied amount of adsorbent was added from 0.5gm, 1gm 1.5gm and 2 gm respectively. These three solutions containing different amounts of adsorbent dosage were then again put through the same ordeal of shaking, centrifuging and spectrophotometer analysis. And the results were used to study the effect of the dosage of adsorbent on the dye removal.

3.2.3.4 Study of Initial dye concentration

Typical dye solutions with varied concentrations ranging between 10-40 mg/L were prepared by dilution to be used as working solutions. To all these solutions, 1gram of orange peel powder was added as adsorbent. The pH of the solutions was maintained at 4.5.

3.2.3.5 Study of temperature

100ml solutions having the same concentration 20mg/l were prepared from the stock solution by dilution. To all these three solutions, 1gm of orange peel adsorbent was added and they were maintained at pH 4.5.The solutions were kept for shaking at 120 rpm for 2hours but at different temperatures of 20, 30 and 40 degrees Celsius respectively. After the completion of 2 hours, they were removed from the shaker ,centrifuged at 8000rpm for 10 mins and then analyzed by the UV-spectrophotometer. In all these study of different parameters, the amount adsorbed is calculated as:

$$q_e = \frac{C_0 - C_e}{X} \qquad (3)$$

q_e = Amount of dye adsorbed per unit mass of adsorbent (mg/g).

C_0= Initial dye concentration (mg/L).

C_e= Final dye concentration (mg/L).

X = Dose of adsorbent (g/L).

Also the removal efficiency is
calculated as :

$$\% \text{ Removal} = \frac{\text{Initial absorbance} - \text{Final absorbance}}{\text{Initial absorbance}} * 100$$

3.2.4 Adsorption Isotherms

Adsorption phenomena is typically represented through isotherms, that is, the amount of adsorbate on the adsorbent as a function of the adsorbate pressure (in case of gas) or concentration (in case of liquid) at a constant temperature. Amount of adsorbate adsorbed is nearly continuously normalized by the mass of the adsorbent to allow comparison of various materials. Studies relating to equilibrium on adsorption process provide data on the capacity of the adsorbent. Also, an adsorption isotherm is characterized by some particular constant values that exhibit the properties of the surface and affinity of the adsorbent and can even be used to compare the adsorptive capacities of that particular adsorbent for various pollutants. The most common model at constant temperature for this sort of adsorption is the Langmuir or Freundlich model.

3.2.4.1 Langmuir Isotherm

Assumptions of Langmuir Isotherm are:

1) The surface available of the adsorbent for adsorption is uniform, that is, all the sites available for adsorption are equivalent.
2) No interaction exists between molecules of adsorbed materials.
3) All sorts of adsorption employ the same mechanism.
4) Only a monolayer is assumed to be formed at the site of maximum adsorption, i.e. molecules of adsorbate do not deposit on another molecules of adsorbate which are already adsorbed. Instead, they only deposit on the available surface left for the adsorption

$$\frac{C_e}{q_e} = \frac{1}{q_m} \cdot \frac{1}{K_L} + \frac{Ce}{q_m} \qquad (5)$$

Ce-concentration at equilibrium

q_e- amount of adsorbate adsorbed per gram of adsorbent at equilibrium;

q_m- Langmuir constants related to adsorption capacity

K_L- Langmuir constants associated with energy of adsorption,

The Langmuir constants qm and KL are calculated from the slope and intercept of plot between Ce/qe *vs* Ce.

3.2.4.2 Freundlich Isotherm

Freundlich isotherm theory describes the quantitative relationship i.e. the ratio of the quantityof adsorbate adsorbed onto a given adsorbent to the concentration of the adsorbate in the solution. It is applicable to adsorption on heterogeneous surfaces and can be denoted by an equation in linear form as:

$$Log\, q_e = Log\, K_f + \frac{1}{n_f} Log\, C_e \qquad (6)$$

The plot of Log q_e versus Log C_e provides the slope $1/n_f$ and intercept K_f ((mg/g)/ $(L/g)^n$))K_f isthe Freundlich constant and n_f is the Freundlich exponent. Here, K_f and n_f are defined as the constants for the adsorption capacity and intensity of adsorption respectively.

3.2.5 Desorption Studies

The study of desorption process helps to understand the mechanism of adsorption and also sheds light on the scope of recovery of adsorbate as well as adsorbent. If the adsorbent is can be successfully regenerated, then it will make the treatment process more economically feasible. A dye solution of 20mg/L was set in two different flasks with adsorbent dose of $0.1gL^{-1}$. The prepared solutions were kept in the shaker for a period of 2 hrs and the final readings were noted down after the attainment of equilibrium. The separation of adsorbent was done by the centrifuge and the obtained sample was dried for 10-12hrs in a hot air oven. After the drying of the adsorbent having adsorbed dye sufficiently, they were put in distilled water at different pH. The final readings of concentration were noted down.

3.3 Characterization of sample

3.3.1 Proximate Analysis

3.3.1.1 Moisture Content

A crucible with its lid was taken and weighed. 1gram of the orange peel adsorbent was taken in the crucible with lid and weighed. It was kept in hot air oven at 100^oC for one and half hours. It was taken out and kept in the desiccator. Then the weight was measured.

$$M = 100 \times \frac{(B-F)}{(B-G)}$$

(10)

Where,

M-moisture content

G- Mass of crucible with lid

B- Mass of crucible with lid plus sample

F- Mass of crucible with lid plus dried sample

3.3.1.2 Ash content

A crucible was taken and weighed. 1gm of the orange peel adsorbent was taken in crucible and weighed. The sample was kept in a muffle furnace for an hour and half at a temperature of 6500C. Then it was taken out and kept in a desiccator for 30 minutes to cool down. Then again the weight is measured.

$$A = 100 * \frac{(F-G)}{(B-G)} \quad (14)$$

Where,

G- Mass of empty crucible

B-mass of crucible plus sample

F-mass of crucible plus ash sample

3.3.1.3 Volatile Matter

A crucible with lid was taken and weighed. 1 gram of sample was taken in the crucible with lid and weighed. It was kept in the muffle furnace at a temperature of 910^{o}Cfor 7 minutes. Then it was taken out and kept in the desiccator for half an hour to cool down. The weight of the sample in crucible with lid was taken.

% Volatile matter was then calculated as,

$$V = 100 * \frac{100(B-F)-M*(B-G)}{(B-G)*(100-M)} \quad (15)$$

3.3.1.4 Carbon Content

Carbon content is calculated as following:

$$\%\text{Carbon} = 100 - (\%\ \text{moisture content} + \%\text{volatile content} + \%\ \text{ash content}) \quad (16)$$

3.3.2 BET Analysis

Brunauer-Emmett-Teller (BET) Surface Area Analysis helps in the precise estimation of the specific surface area of sample. In this, by multilayer adsorption of nitrogen is measured as a function of the relative pressure. A fully equipped and automatic operated analyzer is available for this.It gives the idea of physical adsorption of gas molecule on the solid surface using absorption of N_2 gas on the solid material. This is based on Langmuir's adsorption theory of monolayer adsorption to multilayer adsorption based on the following three postulates:

- The physical adsorption of the gas molecule on the solid layer not definite.
- The adsorbed layers have no interaction with each other.
- Applicability of Langmuir's adsorption theory on each layer.

In this work, BET analysis of the sample i.e the orange peel gave its surface area and pore size and volume values.

3.3.3 Scanning Electron Microscopy

Scanning Electron Microscope is an electron microscope that produces pictures of the solid surface by using a beam of electrons to scan it. The electron beams strike the atoms of the sample surface generating various signals. These signals are detected by electron detector. These signals carry details about the composition and surface structure of the sample. Only the samples of suitable size can be used since they have to be placed in a chamber which only fits the specific size samples. Electrical conductivity of the surface is the most important criterion for SEM characterization of samples. The sample is prepared by coating it with gold to avoid any possible chances of ionization of the sample.

Chapter 4
Results and Discussion

4.1 CHARACTERISTICS OF ADSORBENT

The various physical characteristics of the object were investigated This included proximate analysis to find out the moisture, volatile matter, ash content and fixed carbon percent of the orange peel sample

4.1.1 Proximate Analysis

Proximate analysis was performed for orange peel sample to know its different characteristics and the amount of carbon it contains. It shows very less moisture content(2.5%) and volatile matter and ash content were reported to be 30.25% and 31% respectively. The carbon content is reasonably good enough to make orange peel as a good low-cost adsorbent.

4.1.1 Moisture Content

From equation 13,

$$M = 100 \times \frac{(B - F)}{(B - G)}$$

We have, G=36.40

B=38.40

F=38.35

So Moisture content comes out to be 2.5%. which is reasonably low as compared to similar proximate analysis studies carried out during study of the application of orange peels as adsorbent for other dyes [38]

4.1.2 *Ash content*

From equation 14

$$A = 100 * \frac{(F-G)}{(B-G)}$$

Here, G=36.80, B=38.80, F=37.42

So, Ash content is calculated to be 31 %. Ths is slightly high for orange peels.It indicates that the adsorbent has a lot of mineral matter residue besides carbon which is not combustible

4.1.3 Volatile Matter

Equation 15 gives,

$$V = 100 * \frac{100(B-F) - M*(B-G)}{(B-G)*(100-M)}$$

B=39.1, F=38.46, M=2.5, G=37.1

So, % Volatile matter was 30.25% which is on the slightly lower side indicating less pores for adsorption

4.1.4 Carbon content

By difference we obtain the fixed carbon to be 34.4%.

Table 3:Proximate analysis results.

CONTENT	PERCENTAGE
Moisture content	2.5
Volatile matter	30.25
Ash content	31.0
Carbon	36.25

4.1.2 BET Analysis

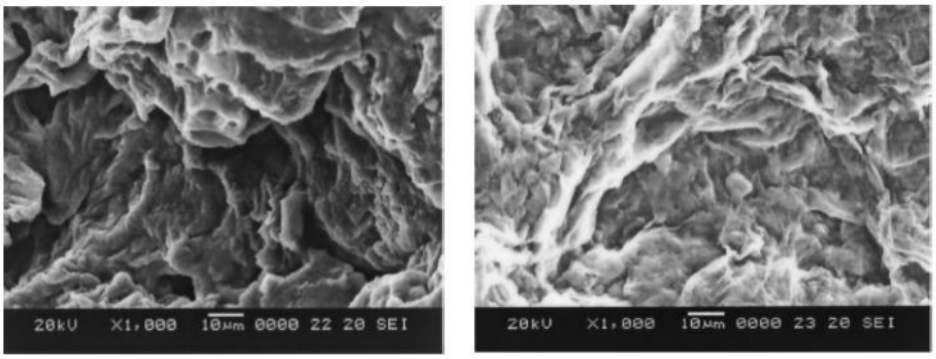
The following tabulated results have been obtained for the case of Orange peel. Table 8 gives values of some of the physical properties which were determined by BET. The N_2 adsorption gave the surface area value(0.7812 m^2/g) which is close to the values as recorded in literature for orange peels[27].

Table 4: BET result for Orange peel.

Properties	Magnitude	Literature [26]
Surface area (m^2g^{-1})	0.7812	0.8311
Total Pore volume (cm^3g^{-1})	0.000541	0.000246
Pore diameter (nm)	2.362	2.3699

4.1.3 SEM Analysis

The SEM images of orange peel sample before and after adsorption of congo red dye have been shown in the figure 9(a) and 9(b) respectively. The orange peels have considerable number of pores for adsorption of dye onto them. Pores within the orange peel particles are heterogeneous before adsorption of dye which is depicted in the image 9(a). After congo red dye is adsorbed on orange peel, a significant change is observed in surface topography of the peels. The original orange peels have a highly porous structure whereas peels have a surface partially covered by dye compounds for the used peels as reflected in figure 3(a) and 3(b).



(a) (b)

Fig 3 (a) SEM image of orange peel sample before adsorption (b) SEM image of orange peel sample after adsorption

4.2 ADSORPTION STUDIES:

4.2.1 Effect of Contact Time

The impact of contact time on adsorption of congo red dye can be seen from Fig.2.It is clearly depicted in the figure that the rate of adsorption is very high initially. But at later stages, the rate of adsorption decreases. The concentration of dye nearly remains constant after 120 minutes. This sets

the equilibrium time for adsorption as 2 hrs or 120 minutes. It is chiefly because of the saturation of these active sites on the orange peel powder which do not permit furthermore adsorption to occur.

This can be explained by the fact that initially, the quantity of sites on the surface are very large which allows adsorption to take place very easily. But with the passage of time, the active sites get saturated thereby reducing the rate at which adsorption occurs. This is more efficient than coir pith which reaches equilibrium at 50% for the same dye concentration of 20 mg/L[36].

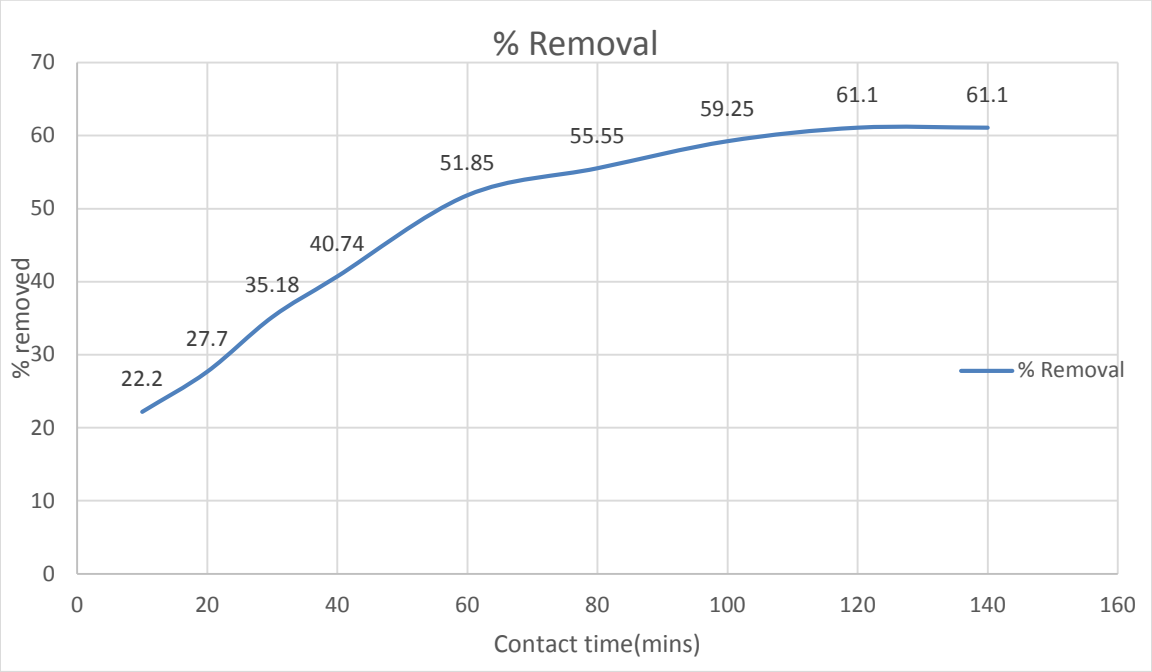


Fig.2.Effect of contact time on the removal of congo red by Orange peel sample

4.2.2 Effect of the Initial pH of the solution:

The original pH of the colorant solution has a very noteworthy impact on the adsorbent's surface characteristics as well as the degree at which the dye molecules ionize. Thus it becomes paramount to examine the impact that pH has on the adsorption process. Figure 3 shows the effect of initial pH on the amount of dye solution adsorbed by orange peel sample.

In the trial, 100ml of 20mg/L dye solutions in the pH range 3-10 have been studied. The pH of the solutions were changed to a desired value by using 0.1N sodium hydroxide (NaOH) and 0.1N hydrochloric acid (HCL) solution utilizing a pH meter. The show that the removal efficiency of dye is reasonably high in a low pH range 3 and below and declined at higher pH. The higher

adsorption at very acidic media could be due to the interactions between the positively charged dyes cations with surface functional groups present in orange peels. On the contrary, at higher pH values, the adsorption decrease which may be because of the formation of soluble hydroxyl complexes. This shows a similar trend with bagasse fly ash and coir pith used as adsorbent [36],[37]

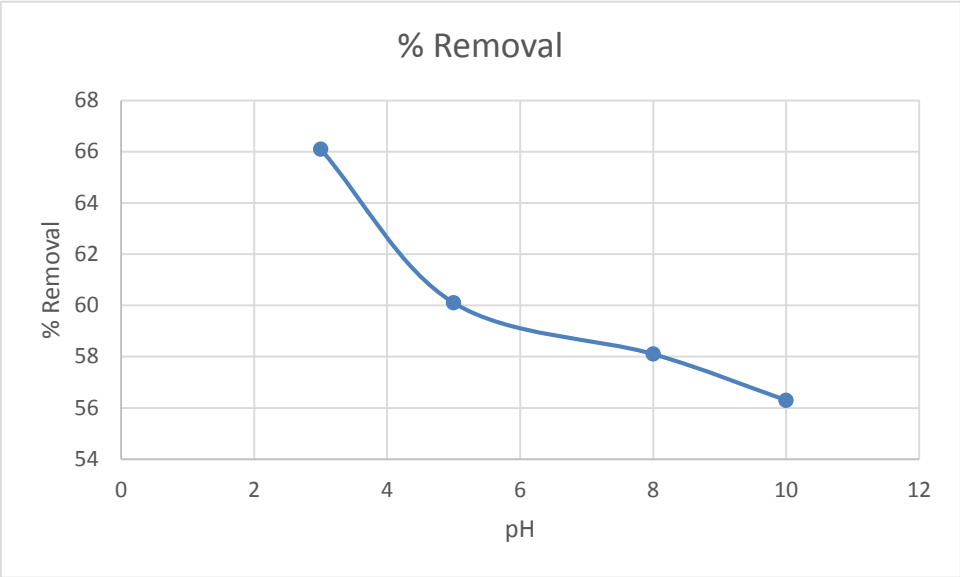


Fig. 3 Effect of initial pH of solution on congo red removal by orange peel adsorbent

4.2.3 Effect of Adsorbent Dosage

The effects of adsorbent i.e. orange peel sample dosage on the amount of dye removed expressed as percentage at initial concentration of 20mg/l at 30^0 c e l s i u s was studied for different dosage of 2g,1.5g, 1g , 0.5g in a solution of volume 100ml. Figure4 depicts that the percentage removal of dye increases with increase in the dosage of adsorbent till there is no further increase in the the amount of colourant removed. Inter particle attraction or reduction of free surface area by overcrowding can be attributed to be the cause of this. Coir pith was used in exorbitantly high amounts for the removal of congo red. This resulted in increased % removal as compared to our studies however as we have established the fact that there are problems in

disposal of the spent adsorbent and regeneration of the adsorbent or recovery of the dye is of paramount importance we can establish the fact that we would generate less wastes from our process. The desorption part will be undertaken subsequently

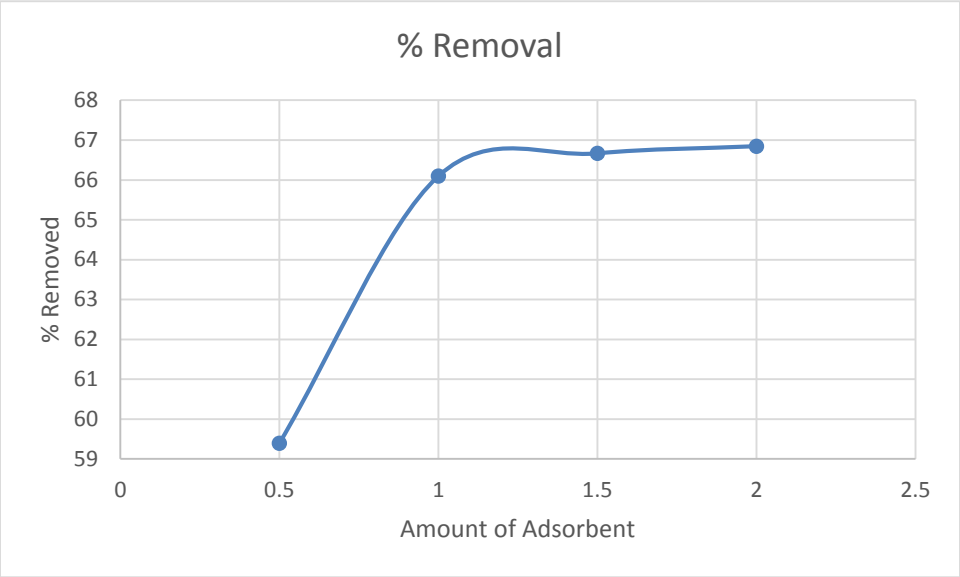


Fig.4 Effect of adsorbent dosage on the dye removal by congo red solution

4.2.4 Effect of initial dye concentration

The concentration of the dye initially has an seeming influence on its exclusion from aqueous phase. The effect of congo red dye concentration on the efficacy of adsorption was also explored

in the initial concentration range of 10-40 mg/L. as shown in figure 5.The adsorption capacity of orange peel at equilibrium seems to increase with increase in the concentration of the initial dye concentration. This trend could be attributed to the fact that because of the high concentration of the dye, the driving force for mass transfer is also relatively high. Additionally, if the concentration of dye in the solution is higher, the active sites are enclosed by more dye molecules which leads to more efficient adsorption. Both coir pith and bagasse fly ash showed similar trends however the trend in coir pith didn't flat line and continued to rise up for higher subsequent values of adsorbent mass taken

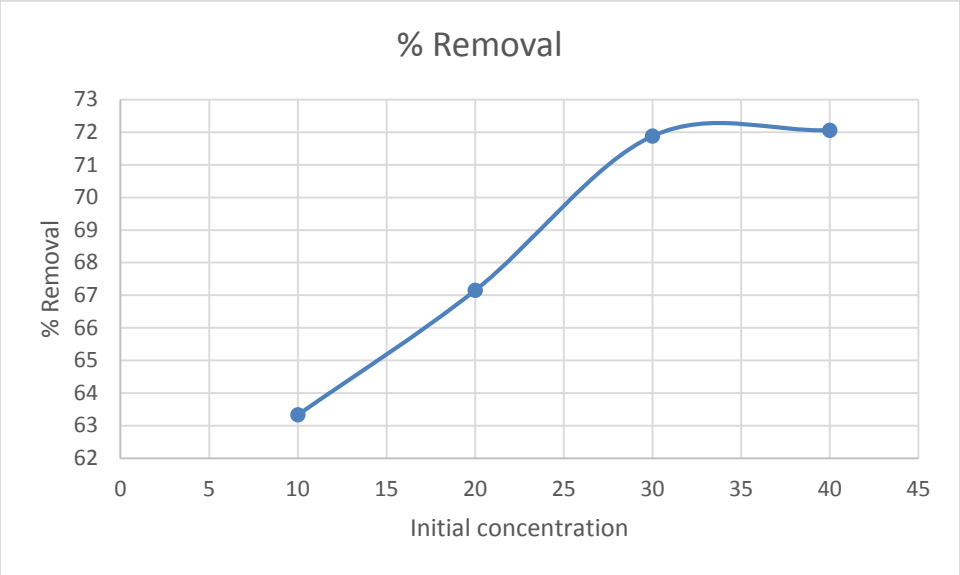


Fig. 5 Effect of initial dye concentration on the removal of congo red by orange peel adsorbent

4.2.5 Effect of Temperature

Temperature is not a very important controlling factor in this study of the applications of adsorbent for the dye removal process. Figure 6 represents the adsorption of congo red by orange peel at different values of temperatures. The temperature doesn't affect the reduction in dye concentration by much however there is a slight increase increase in the adsorption which means that the chemical interactions that take place between congo red dye and the adsorbent is endothermic in nature. Pith and bagasse fly ash showed similar trends [36][37]

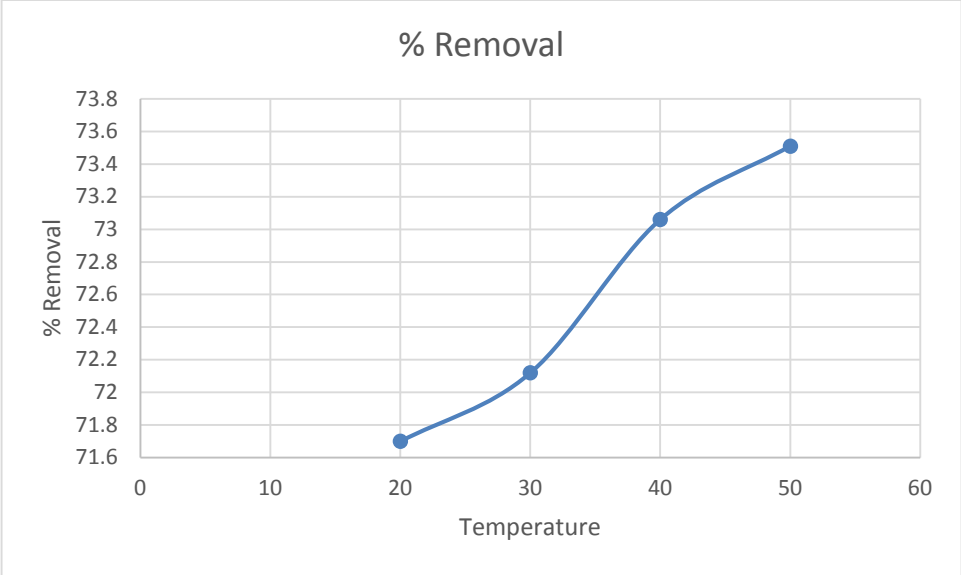


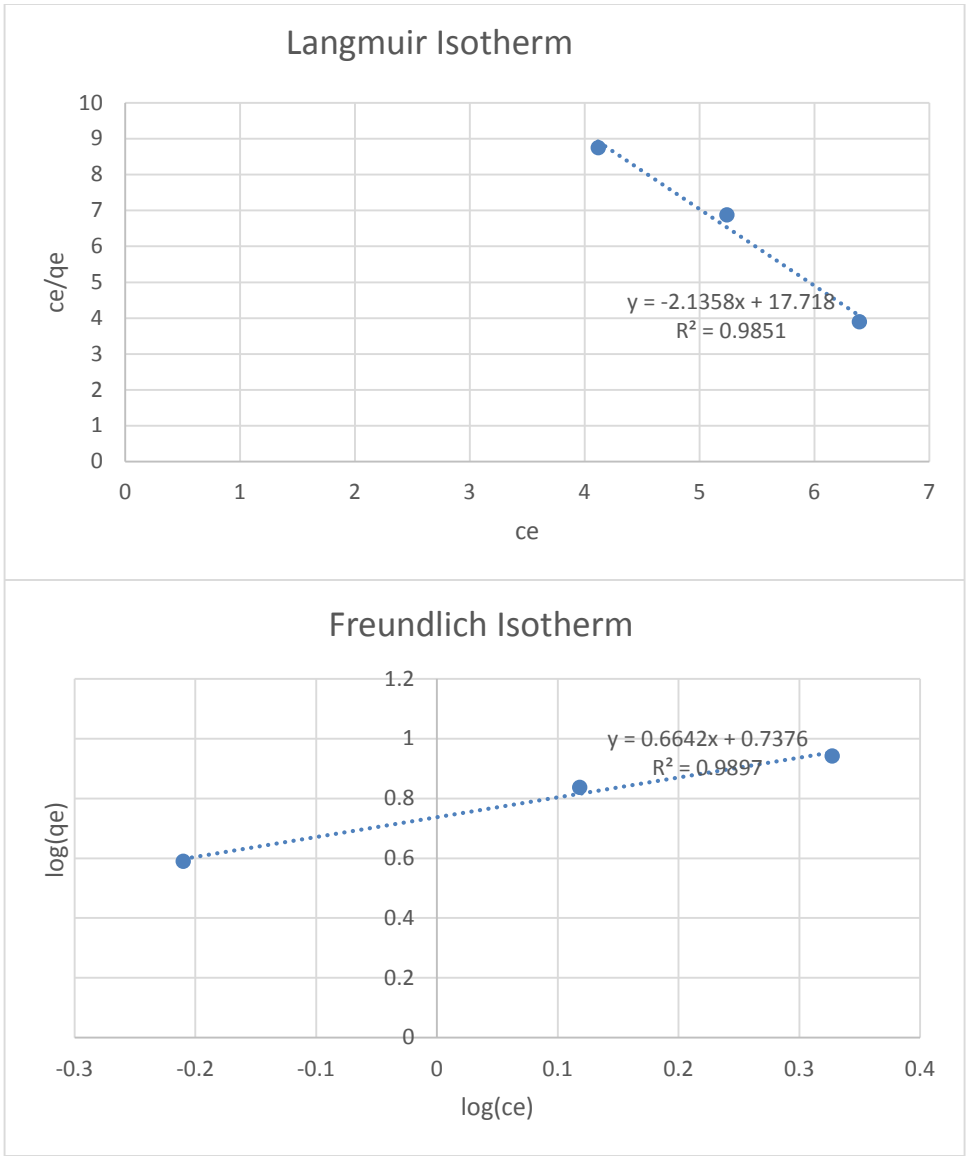
Fig. 8 Effect of temperature on the removal of congo red dye by orange peel adsorbent

4.3 ADSORPTION ISOTHERMS

The values of the constants of the two isotherms, namely, Freundlich and Langmuir, have been given in the table below. The values for Freundlich and Langmuir isotherm are 0.9851 and 0.9567 respectively for the adsorption of congo red. It is clearly noticeable that Freundlich model is better fit in the adsorption isotherm model (Table 6).This shows that adsorption of the dye follows heterogeneous polylayer coverage of the adsorbate on the adsorbent surface.

Table 6: Evaluated adsorption constants at different Isotherm models:

	Langmuir Isotherm			Freundlich Isotherm		
Adsorbant Dosage	K_L	q_m	R^2	K_f	1/n	R^2
1g	0.06	18.94	0.9851	2.236	0.501	0.9567

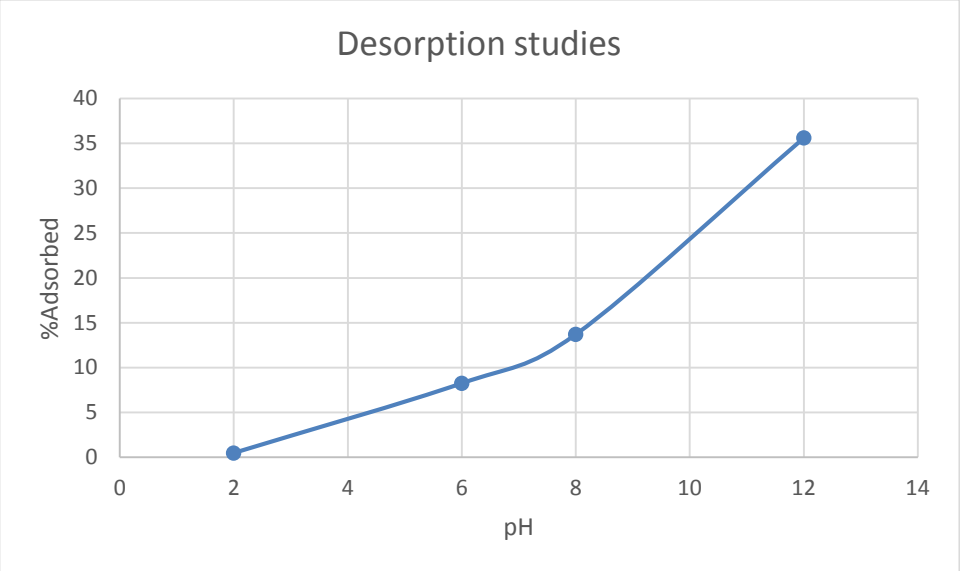

Langmuir Isotherm
ce/qe
ce
y = -2.1358x + 17.718
R² = 0.9851
Freundlich Isotherm
log(qe)
log(ce)
y = 0.6642x + 0.7376
R² = 0.9897

4.4 DESORPTION STUDY:

The desorption study has been performed to find out the scope of recovery of dye after the project. The study was conducted at different ranging from low to high. With an increase in pH of the aqueous medium, the amount of desorption is also increased. This is just opposite to the pH effect. It was observed that maximum desorption occurred at higher pH. Thus recovery and recycle of adsorbate as well as adsorbent might be possible. This is where orange peel beats the other two adsorbents. While coir pith could manage a maximum recovery of 11% we were able to achieve 3 times that at a very alkaline pH [36].

Table 7: Desorption results

pH	Percentage of dye desorbed
2	0.48
6	8.25
8	13.7
12	35.6



Chapter-5
Conclusion

5. CONCLUSIONS

Removal of congo red dye from aqueous solution using orange peel as adsorbent was experimentally determined and these observations are made:

1. Proximate analysis showed good carbon content which favors adsorption. Percentage carbon was found to be 36.25%.The moisture content (2.5%), volatile content and ash content were also found to be quite reasonable.
2. Scanning Electron micrographs exhibited that orange peel had a significant number of pores where there is a feasibility for congo red dye to be trapped and adsorbed into these pores and also there is change in the surface characteristics of orange peel before and after adsorption of the dye.
3. Adsorption tends to increase with time of contact. This is because with time the number of free sites for adsorption keep on decreasing as more and more of the adsorbate gets adsorbed until saturation is reached.. The optimum contact time for equilibrium was found to be120 mins or 2 hours.
4. The removal efficiency of adsorbent is increases with decrease of Ph. In the acidic media, the electrostatic interactions between the adsorbent that is positively charged and negatively charged dye anions whereas at higher pH values the more number of negatively charged anions reduces the dye adsorption due to electrostatic repulsions.
5. As adsorbent dose increases adsorption increases due to the availability of more number of free sites.1g/100ml concentration of adsorbent is taken as the optimum adsorbate dose. As we increase adsorbate dose more than the optimum the increase in adsorption is very less and it becomes cost ineffective.
6. There is surge in adsorption with the increase in initial concentration of dye due to the higher driving force for the transfer of mass at a higher initial dye concentration.
7. Adsorption capacity is found to increase with increase in temperature. At higher temperature mobility of large ions of congo red dye increases and at high temperature molecules acquire sufficient energy to undergo interaction with the active sites for adsorption.

8. The adsorption process follows pseudo-first-order kinetics and the thermodynamic studies showed that that the process is feasible and spontaneous
9. Although the experimental equilibrium data fitted well to Langmuir as well as Freundlich isotherm equations, the Langmuir Isotherm model fitted the best.
10. Desorption studies showed that the recovery and recycling of adsorbent as well as the adsorbate might be possible.

Thus it can be concluded that orange peels, which are waste materials and are in abundance in the country, can be used for the removal of congo red dye from waste water. Further, there is scope of more study and research which can enhance the percentage removal of congo red and also, the feasibility of orange peels for removal of other dyes is to be studied.

Chapter-6
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